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**(54) Process for making controlled uniform-sized polymer particles**

Verfahren zur Herstellung von Polymerteilchen mit kontrollierter, gleichförmiger Teilchengröße

Procédé pour la fabrication de particules polymériques à taille uniforme contrôlée

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• **Database WPIL, N 86-160411, Derwent**  
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**EP 0 448 391 B1**

## Description

The present invention is concerned with a polymerization process, and more particularly to a process for polymerizing water-insoluble monomers in the presence of pre-formed, uniformly sized polymer particles.

Small polymer particles, in the range of 1 to 50 micrometers ( $\mu\text{m}$ ), have many applications, including light scattering and diffusion, surface coating, intermediates for preparation of chromatographic solid phases, adsorbents, and ion-exchange materials. For many such applications, particularly optical and chromatographic applications, uniformity of the particle size is critical to performance. Emulsion polymerization can produce particles up to about 0.5 to 1.0  $\mu\text{m}$  having a relatively narrow size distribution, but the size is limited by the nature of an emulsion. In such a polymerization the monomers are emulsified in water using a soap, and the polymerization is initiated by a water-soluble, free-radical initiator. The particle size depends more on the composition of the polymerization mixture, *i.e.*, the soap, the stabilizers used and the monomers themselves, than on the specific physical conditions of the polymerization.

Suspension polymerization can produce particles from about 50  $\mu\text{m}$  to about 2 mm. The monomer is suspended as droplets in water, and polymerization is initiated by an oil-soluble initiator which partitions into the monomer droplets. Particle size depends on the size of the monomer droplets, which is affected primarily by the stirring rate, the amount of suspension stabilizers, and similar physical conditions for the polymerization. As a result of the inherent variability of these conditions, particle size distribution tends to be broad. Smaller particles, *e.g.* as small as 10  $\mu\text{m}$ , have been reportedly produced by high-shear suspension polymerization, but the size distribution is even broader.

Grinding of polymers that have been made by other processes which produce larger sized polymers, such as bulk polymerization, can lead to particles in the desired size range. Unfortunately, grinding not only results in large size distribution, but causes thermal degradation of heat-sensitive polymers. Thus direct production of particles larger than 1  $\mu\text{m}$  but smaller than 50  $\mu\text{m}$  is difficult.

Derwent Abstract 86-160 411, which refers to JP-A-61095016, describes an electrode spacer for an LCD device, the spacer comprising a polymer obtained by absorbing an oleophilic substance into a seed polymer particle dispersed in an aqueous dispersion medium, followed by absorbing a monomer and then polymerizing the absorbed product by an oleophilic polymerization initiator.

Multiple-step processes have been used to produce particles within the range of 1 to 50  $\mu\text{m}$ . In these processes a pre-formed emulsion polymer, or "seed", is used as a starting material. The polymer is swollen, either in an organic solvent or in a monomer which behaves as a swelling solvent for the polymer, and monomer is im-

bibed into the swollen structure of the polymer and polymerized there, thus increasing the size of, or "growing", the particle. This swelling, imbibing and polymerizing process may be repeated to further increase the size of the particle. Because the emulsion polymerization that forms the seed inherently produces a relatively narrow size distribution, the multiple-step processes have the potential for producing larger particles with similarly narrow size distributions. Not all multiple-step processes live up to this potential, and the swelling and imbibing steps are inherently slow; the reactions may take days. In addition, those processes which involve swelling solvents introduce the economic and environmental problems of solvent recovery and disposal. Special low-shear agitation or highly dilute dispersions may also be required to prevent the particles from coalescing during growth.

The present invention enables a rapid, solvent-free process to be provided by which polymer particles in the size range of 1 to 50  $\mu\text{m}$  and having a narrow size distribution may be made.

According to the present invention there is provided a process for making uniformly sized polymer particles having a selected final particle size within the range of 1 to 50  $\mu\text{m}$ , which comprises the steps of:

- a) combining a free-radical-polymerizable, water-insoluble monomer or mixture of such monomers with an aqueous dispersion of uniformly sized seed polymer particles until sufficient of the monomer or mixture of monomers has been combined to grow the particles to a selected size, and wherein the monomer or mixture of monomers is combined with the aqueous dispersion of seed polymer particles (i) in the presence of a dispersion stabilizer and an oil-soluble, free-radical polymerization initiator, (ii) at a temperature at least as high as that at which the initiator is activated, and (iii) at a rate such that an amount of the monomer or mixture of monomers equal to the total initial weight of the seed polymer particles would be combined with the dispersion over a period of from 45 to 120 minutes; and
- (b) maintaining the temperature of the combined monomer(s) and particles at least as high as that at which the initiator is activated until all the monomer is polymerized,

these steps, optionally, being repeated until the selected size is equal to the selected final particle size.

The porogen may, for example, be used in an amount of up to 50%, the percentage being based upon the weight of the monomer(s) plus porogen.

In the process of the present invention the uniformly sized seed polymer particles, *e.g.* emulsion polymerized particles, are swollen by the monomer, which is polymerized to become part of the seed particles and permanently increase their size. Because the seed particles have a uniform size, and the conditions affecting uptake

of monomer by the particles are relatively uniform throughout the reaction mixture, the size of the product particles depends primarily upon the amount of monomer combined with the seed particle dispersion. The stabilizing agent (i.e. the dispersion stabilizer) inhibits coalescence of particles in the dispersion, thus helping preserve particle-size uniformity. The use of an oil-soluble (water-insoluble) initiator helps inhibit formation of new emulsion particles and promotes the growth of the seed particles, because it partitions into the monomer-polymer phase found in the particles and thus tends to be unavailable to monomer in the aqueous phase.

Yet another important factor in avoiding new emulsion particles, and in preventing agglomeration of existing particles, is the rate at which monomer is combined with the particles. In a preferred embodiment of the invention, wherein monomer is fed to the dispersion of particles, the feed rate is such that at least 45 minutes is required to add a weight of monomer equal to the initial weight of the seed particles, and preferably such that the free monomer in the dispersion is no more than 10% of the particle weight at any time during the process.

Emulsion-polymer seed particles useful in the process of the present invention may be prepared by emulsion polymerization processes known to those skilled in the art. Such processes inherently produce particles of relatively narrow particle-size distribution; one skilled in the art will understand how to vary the emulsion polymerization conditions to produce particles having a mean particle diameter within the range of 0.01 to 2  $\mu\text{m}$ . Seed particles within this size range, and more preferably in the range of 0.05 to 0.5  $\mu\text{m}$ , may be used in the present process. The seed particles may be crosslinked or uncrosslinked. The monomers from which they may be prepared include vinylaliphatic monomers such as esters of acrylic and methacrylic acids, and acrylonitrile, olefins such as ethylene and propylene, and aliphatic monomers with conjugated unsaturation such as butadiene. They may also be prepared from vinylaromatic monomers such as styrene, and substituted styrenes. The seed particles may be crosslinked by the formation of secondary crosslinks within the polymer structure, by the inclusion of a polyethylenically unsaturated monomer or monomers among the monomers from which the seed particles are formed, or by any other crosslinking processes known to those skilled in the art. Preferred seed particles are crosslinked copolymers of styrene with divinylbenzene.

The suspending agent for the process of the present invention is water. The stabilizing agents useful for the process are preferably anionic surfactants, for example alkyl, aryl or alkaryl sulfates, sulfonates, phosphates or succinates, and their ethoxylated derivatives, nonionic surfactants, for example polyoxyethylene alkyl ethers, polyoxyethylene alkyl phenol ethers, or polyethylene glycols, or mixtures of anionic and nonionic surfactants. Water-soluble polymers such as polyvinyl al-

cohol, polyvinylpyrrolidone, carboxyalkyl celluloses and hydroxyalkyl celluloses may also be incorporated into the polymerization mixture for additional stabilization of the latex particles.

The initiator useful for the process of the present invention is an oil-soluble, free-radical initiator, and preferably has a one-hour half-life temperature of 60° to 100°C. The one-hour half-life temperature is readily understood by those skilled in the art as that temperature at which one half of the initiator present at any given time will have decomposed, forming free radicals, within one hour. The preferred initiators are peroxides such as t-butyl peroctoate and benzoyl peroxide, preferably benzoyl peroxide, and azo initiators such as 2,2'-azobis (2-methylbutane nitrile) and 2,2'-azobis(2,4-dimethylpentane nitrile). The preferred initiator concentration is from 0.5% to 2% by weight of the total monomer. The temperature of the polymerization is at least the activation temperature of the initiator selected, and is preferably from 50° to 90°C. The activation temperature of the initiator is readily understood by one skilled in the art to be the lowest temperature at which the initiator begins to decompose and generate a significant concentration of free radicals. The preferred reaction pressure is atmospheric but the reaction will proceed at pressures above and below atmospheric where some other advantage justifies the additionally complex equipment that non-atmospheric polymerization requires.

The monomers useful in the present invention are any water-insoluble, free-radical-polymerizable monomers or mixtures of such monomers. Preferably, the monomer or mixture of monomers is one or more vinylaromatic monomers, and particularly preferred is styrene. The monomer or mixture of monomers may include crosslinking monomers, that is, monomers containing more than one polymerizable functional group, for example divinylbenzene, and graftlinking monomers, that is, those monomers containing more than one polymerizable functional group in which the polymerizable functional groups polymerize at significantly different rates, for example allyl methacrylate.

The polymer particles of the present invention may be made in either a microporous or a macroporous form. The microporous particles, often referred to as "gel" particles, contain only the intermolecular porosity of the polymer itself, with pore diameters in the range of from 0.1 to 5 nm, while the macroporous particles contain an additional porosity which is independent of the intermolecular porosity, with pore diameters beginning at 5 nm and ranging upwards to as large as 10  $\mu\text{m}$  in large polymer particles, and proportionally smaller in smaller particles, e.g., particles of 10  $\mu\text{m}$  may have pores with diameters as large as about 1  $\mu\text{m}$ . When a porogen is absent from the monomer or mixture of monomers added to the seed particles, the resulting polymer particles will be merely microporous, but when a porogen is included, the particles will be macroporous. Polymerization in the presence of a porogen to produce macroporous poly-

mers is, for example, described in U.S. - A - 4,382,124; the porogens are referred to therein as "polymer precipitants" or merely "precipitants". The porogen is characterized by being a solvent for the monomer mixture being copolymerized while exerting essentially no solvent action on the copolymer. Introduction of the porogen to the monomer phase decreases the solubility in the monomer phase of any copolymer formed, causing the polymer to separate from the monomer phase as it is formed, a phenomenon known as "phase separation". As the concentration of monomer in the polymerizing mass decreases because of polymerization, and as the concentration of resulting copolymer increases, the porogen is more strongly repelled by the copolymer mass and is actually squeezed out of the copolymer phase leaving a series of interconnecting pores that are large relative to the intermolecular micropores. Suitable porogens for use in the process of the present invention include: C<sub>4</sub> to C<sub>10</sub> alkanols such as butanol, and linear and branched pentanols, hexanols, heptanols, octanols, nonanols and decanols, for example 4-methylpentan-2-ol (methyl isobutyl carbinol); C<sub>7</sub> to C<sub>20</sub> saturated aliphatic hydrocarbons; alkyl esters of seven or more carbon atoms, such as n-hexyl acetate, 2-ethylhexyl acetate, methyl oleate, dibutyl sebacate, dibutyl adipate and dibutyl carbonate; aliphatic ketones such as methylisobutylketone, diisobutylketone; and aromatic hydrocarbons such as toluene and ortho and para xylenes. The specific kind and percentage of porogen in the monomer mixture is selected according to the degree of macroporosity desired and the particular monomers. US - A - 4,382,124, mentioned above, may serve as a guide to this selection.

In one embodiment of the present invention the porogen is toluene, xylene, or methyl isobutyl carbinol.

The size to which the polymer particles are grown according to the present invention is determined by the amount of monomer or monomer mixture used. Typically, monomer may be combined with the polymer particles until they have grown to about 10 times their initial volume, and more preferably about 7 times their original volume, although it is clear that using less monomer will result in a smaller product, and the desired particle size may be selected by one skilled in the art to be suitable for the particular use contemplated for the final particle. The selected particle size is preferably within the range of from 1.1 to 10 times the initial particle volume, more preferably from 1.5 to 7 times the initial particle volume, and still more preferably from 2 to 5 times the initial particle volume. It is clear from simple geometry that a change in volume produces a diameter change that is the cube root of the volume change, i.e., a 5x volume is a  $\sqrt[3]{5}x$  diameter change, or a 1.71x diameter change.

The above discussion of the size to which the particles may be grown refers to a single application of the present process. Particles much larger than a 10-fold volume increase may be obtained by repeating this process using as seed particles the product particles

from this process. By such repetition, particles may be grown that are significantly larger than those obtainable from a single growth step. Seed particles in the preferred diameter range of 0.05 to 0.5  $\mu$ m may thus be grown to any diameter within the range of 1 to 50  $\mu$ m by from one to ten or more repetitions of this process.

In one embodiment of the present invention the seed polymer particles are particles produced by applying steps (a) and (b) to emulsion-polymerized particles one or more times.

In combining the monomer and the suspension of seed polymer particles, it is clear that the monomer may be added to the suspension, the suspension may be added to the monomer, or both may be added simultaneously to one another in a separate vessel. Addition of the monomer to the suspension is preferred, and will be used in the following illustrations.

The feed rate for the monomer is such that an amount of monomer equal to the weight of the total original seed particles would be combined with the suspension of polymer particles over a period of from 45 to 120 minutes, and more preferably from 60 to 90 minutes, until the seed particles have grown to the selected size. That is, the feed rate is maintained within this range, and the length of time for the addition is selected so that the desired particle growth occurs.

For example, if a feed rate is selected such that an amount of monomer equal to the weight of the total original seed particles is combined with the suspension of polymer particles over a period of 60 minutes, and a particle volume increase of 5 times is desired, the monomer is fed to the suspension over a 5-hour period. Essentially all of the monomer is polymerized into the existing particles, and as no significant change in particle density occurs, the volume of each particle increases 5-fold.

More preferably, the addition of the monomer or mixture of monomers, e.g. the addition of the monomer or mixture of monomers to the suspension of seed polymer particles, is at a controlled rate such that the free monomer in the reaction mixture does not exceed 10%, by weight, of the instantaneous polymer-particle weight. The instantaneous polymer-particle weight is the total polymerized weight of the particles at any time during the reaction, and includes the polymer mass added to the original seed particles during the polymerization of the present process. The free monomer is that monomer that has been combined with the polymer particles but has not yet reacted at a given time during the process. If the levels of free monomer exceed 10%, the polymer particles may coagulate, which will undesirably increase the particle size and size distribution. Levels of free monomer above 10% may also lead to formation of an additional population of emulsion-sized particles, which will again contribute to an undesirably broad particle-size distribution.

A particularly advantageous feature of the present invention is that it eliminates the need to swell the seed polymer prior to addition of the monomer solution. No

lengthy soaking in an organic solvent is required; the gradual addition of the monomer-initiator solution may, for example, be begun immediately after charging an aqueous suspension of the seed particles to a reaction vessel.

The following Examples are presented to illustrate preferred embodiments of the present invention. All percentages and proportions are by weight unless otherwise specified, and all reagents are of good commercial quality unless otherwise specified.

#### Example 1

This Example illustrates the growth of a polystyrene seed latex having a particle size 3.3  $\mu\text{m}$  into uniformly sized polymer particles of 5- $\mu\text{m}$  diameter with a styrene-3.8% divinylbenzene monomer mixture using the procedure of the present invention.

To a 5-liter, round-bottomed kettle equipped with a condenser, agitator, heating source, inert-gas inlet, temperature sensor and pump-driven feed lines was charged 1860 g deionized water and 20 g of a 30% aqueous solution of sulfated polyethoxynonylphenol, ammonium salt as a surfactant. The mixture was heated under nitrogen to 85°C with agitation. 678 g of a polystyrene seed latex having a particle size of 3.3  $\mu\text{m}$  and a solids content of 35.4% was rinsed into the kettle with 100 g additional deionized water, and the mixture was re-heated to 85°C. A monomer emulsion of 320 g deionized water, 12 g of a 30% aqueous solution of sulfated polyethoxynonylphenol, ammonium salt as a surfactant, 893.5 g styrene, 66.5 g commercial divinylbenzene (55% purity, the balance being largely ethylvinylbenzene) and 9.6 g benzoyl peroxide initiator was prepared and fed into the kettle at a constant rate such that the entire emulsion was transferred to the kettle in 4 hours, a chaser of 1 g benzoyl peroxide initiator dissolved in 5 g styrene being added to the emulsion container after 3.5 hours. The emulsion container was then rinsed into the kettle with 100 g additional deionized water. At the end of the 4-hour emulsion feed, the kettle contents were held at 85°C for one hour, then cooled and filtered through a 45- $\mu\text{m}$  sieve. The solids content of the resulting polymer suspension was 29.4%. The size of the particles was determined by optical microscopy to be 5.6  $\mu\text{m}$  (94% of the particles), with approximately 6% of the particles significantly exceeding this size because of the coalescence of two or three particles.

#### Example 2

The following Example is intended to illustrate the growth of an uncrosslinked polystyrene seed latex from a particle size of 4.9  $\mu\text{m}$  to 8.4  $\mu\text{m}$  using the procedure of the present invention.

Following the procedure of Example 1, 419 g deionized water and 6.4 g of a 30% aqueous solution of sulfated polyethoxynonylphenol, ammonium salt, sur-

factant was charged to the kettle. The kettle contents were heated to 85°C, and 206.9 g of a polystyrene seed latex having a particle size of 4.9  $\mu\text{m}$  and a solids content of 28% was rinsed into the kettle with 30 g of deionized water. A monomer emulsion of 80 g deionized water, 1.6 g of the above surfactant solution, 240 g styrene and 2.4 g benzoyl peroxide was prepared and fed into the kettle at a constant rate over a period of 4 hours. The emulsion container was then rinsed into the kettle with 30 g of additional deionized water. The mixture was held at 85°C for one hour, cooled and filtered. The resulting latex had a solids content of 28.9% and a particle size of 8.4  $\mu\text{m}$ , with approximately 4% of the particles significantly exceeding this size because of the coalescence of two or three particles.

#### Example 3

This Example is intended to illustrate the growth of a lightly crosslinked (0.1% divinylbenzene) seed from a particle size of 8.4  $\mu\text{m}$  to 14.2  $\mu\text{m}$  with a styrene-0.1% divinylbenzene monomer mixture using the procedure of the present invention.

Using the procedure of Example 1 above, a kettle charge of 530 g deionized water, 94 g of a 10% aqueous solution of ammonium octylphenoxyethoxyethyl phosphate surfactant, 13.5 g of a 70% aqueous solution of octylphenoxypropylpolyethoxyethanol nonionic surfactant, and 58.7 g of a 2% aqueous solution of methylhydroxypropyl cellulose was prepared. To this mixture was added 312.5 g of a 99.9 styrene/0.1 divinylbenzene seed latex having a particle size of 8.4  $\mu\text{m}$  and a solids content of 25.6%, with a 30-g deionized water rinse. The mixture was heated to 85°C with agitation under a nitrogen atmosphere, and a monomer emulsion of 152.8 g deionized water, 3.1 g of the above nonionic surfactant, 21.6 g of the above phosphate surfactant, 14 g of 2% aqueous solution of methylhydroxypropyl cellulose, 319.4 g styrene, 0.6 g divinylbenzene and 3.2 g benzoyl peroxide was fed to the kettle at a constant rate over 4 hours. The monomer emulsion container was rinsed into the kettle with 30 g of deionized water and the batch was held at 85°C for one hour, cooled and filtered. The resulting latex had a solids content of 26.7% and a particle size of 14.2  $\mu\text{m}$ , with approximately 8% of the particles significantly exceeding this size because of the coalescence of two or three particles.

#### Example 4

This Example is intended to illustrate growth of a butyl methacrylate seed latex from a particle size of 1.7  $\mu\text{m}$  to 2.9  $\mu\text{m}$  with methyl methacrylate monomer using the procedure of the present invention.

Using the procedure of Example 1 above, the kettle was charged with 403.5 g deionized water, and 222.2 g of a poly(butyl methacrylate) seed latex having a particle size of 1.7  $\mu\text{m}$  and a solids content of 27% was added

to the kettle with a rinse of 30 g deionized water. The mixture was heated to 85°C with agitation under a nitrogen atmosphere, and a monomer emulsion of 80 g deionized water, 1.6 g of a 30% aqueous solution of ammonium sulfated polyethoxynonylphenol surfactant, 240 g methyl methacrylate and 2.4 g benzoyl peroxide was added at a constant rate over a period of 6 hours, then rinsed into the kettle with 30 g deionized water. The mixture was held at 85°C for 45 minutes, then cooled and filtered. The resulting latex had a solids content of 29.2% and a particle size of 2.9 µm, with about 3% of the particles significantly exceeding this size because of the coalescence of two or three particles.

#### Example 5

This Example is intended to illustrate the growth of a mixed butyl methacrylate-styrene seed latex from a particle size of 3.4 µm to 5.4 µm with mixed butyl methacrylate and styrene monomers using the procedure of the present invention.

Using the procedure of Example 1 above, the kettle was charged with 412 g deionized water, 1 g aqueous ammonia and 4.2 g of 0.15% aqueous magnesium *p*-nitrosophenoxide retarder. To this mixture was added 208.3 g of a 65 butyl methacrylate/35 styrene seed latex having a particle size of 3.4 µm and a solids content of 28.8%, with a rinse of 30 g deionized water. The mixture was heated to 85°C with agitation under a nitrogen atmosphere, and a monomer emulsion of 80 g deionized water, 2.4 g of a 30% aqueous solution of sulfated polyethoxynonylphenol, ammonium salt, surfactant, 156 g butyl methacrylate, 84 g styrene and 2.4 g *t*-butyl peroxoate initiator was added at a constant rate over a period of 4.5 hours, then rinsed into the kettle with 30 g deionized water. The mixture was held at 85°C for one hour, then cooled and filtered. The resulting latex had a solids content of 28.6% and a particle size of 5.4 µm.

#### Example 6

This Example is intended to illustrate the growth of a more highly crosslinked (10% divinylbenzene) seed from a particle size of 3.3 µm to 4.6 µm with a styrene-10% divinylbenzene monomer mixture using the procedure of the present invention.

Using the procedure of Example 1 above, the kettle was charged with 442 g deionized water and 12.8 g of a 30% aqueous solution of sulfated polyethoxynonylphenol, ammonium salt, surfactant. To this mixture was added 172.4 g of a polystyrene seed latex having a particle size of 3.3 µm and a solids content of 34.8%, with a rinse of 30 g deionized water. The mixture was heated to 85°C with agitation under a nitrogen atmosphere, and a monomer emulsion of 80 g deionized water, 3.2 g of the above surfactant, 196.4 g styrene, 43.6 g divinylbenzene and 2.4 g benzoyl peroxide initiator was added at a constant rate over a period of 5 hours, then rinsed into

the kettle with 30 g deionized water. The mixture was held at 85°C for two hours, then cooled to 55°C, and a chaser of 2.4 g of a 0.15% aqueous solution of ferrous sulfate, 0.19 g sodium sulfoxylate formaldehyde in 10 g water and 0.41 g of a 70% aqueous solution of *t*-butyl hydroperoxide was added. The mixture was then held at 55°C for 30 minutes, cooled and filtered. The resulting latex had a solids content of 30.9% and a particle size of 4.7 µm with about 0.5% of the particles significantly exceeding this size because of the coalescence of two or three particles.

#### Claims

1. A process for making uniformly sized polymer particles having a selected final particle size within the range of 1-50 µm, which comprises the steps of:

- a) combining a free-radical-polymerizable, water-insoluble monomer or mixture of such monomers with an aqueous dispersion of uniformly sized seed polymer particles until sufficient of the monomer or mixture of monomers has been combined to grow the particles to a selected size, and wherein the monomer or mixture of monomers is combined with the aqueous dispersion of seed polymer particles (i) in the presence of a dispersion stabilizer and an oil-soluble, free-radical polymerization initiator, (ii) at a temperature at least as high as that at which the initiator is activated, and (iii) at a rate such that an amount of the monomer or mixture of monomers equal to the total initial weight of the seed polymer particles would be combined with the dispersion over a period of from 45 to 120 minutes; and
- b) maintaining the temperature of the combined monomer(s) and particles at least as high as that at which the initiator is activated until all the monomer is polymerized,

these steps, optionally, being repeated until the selected size is equal to the selected final particle size.

2. A process as claimed in claim 1, wherein the rate at which the monomer or mixture of monomers and the dispersion are combined is such that the amount of monomer or mixture of monomers equal to the total initial weight of the seed polymer particles is combined with the dispersion over a period of from 60 to 90 minutes.

3. A process as claimed in claim 1 or claim 2, wherein the rate of addition of the monomer or mixture of monomers is such that the free monomer or mixture of monomers present does not exceed 10%, by

weight, of the instantaneous polymer-particle weight.

4. A process as claimed in any preceding claim, wherein the selected size obtained from step (a) is from 1.1 to 10 times, preferably from 1.5 to 7 times, and most preferably 2 to 5 times, the initial volume of the seed polymer particle. 5
5. A process as claimed in any preceding claim, wherein the seed polymer particles are emulsion-polymerized particles having an initial diameter of from 0.01 to 2  $\mu\text{m}$ , preferably from 0.05 to 0.5  $\mu\text{m}$ . 10
6. A process as claimed in any preceding claim, wherein the seed polymer particles are particles produced by applying steps a) and b) to emulsion-polymerized particles one or more times. 15
7. A process as claimed in any preceding claim, wherein the stabilizing agent is selected from anionic surfactants and nonionic surfactants. 20
8. A process as claimed in claim 7, wherein the stabilizing agent additionally includes a water-soluble polymer. 25
9. A process as claimed in any preceding claim, wherein the initiator has a one-hour half-life temperature of from 60° to 100°C. 30
10. A process as claimed in any preceding claim, wherein the initiator is a peroxide initiator, preferably benzoyl peroxide, or an azo initiator. 35
11. A process as claimed in any preceding claim, wherein the monomer or mixture of monomers is one or more vinylaromatic monomers and, optionally, includes crosslinking monomer. 40
12. A process as claimed in claim 11, wherein the monomer is styrene. 45
13. A process as claimed in any preceding claim, wherein the monomer or mixture of monomers is combined with the polymer particles in the presence of a porogen. 50
14. A process as claimed in claim 13, wherein the porogen is present in an amount of up to 50%, the percentage being based on the weight of monomer(s) plus porogen. 55
15. A process as claimed in claim 13 or claim 14, wherein the porogen is toluene, xylene, or methyl isobutyl carbinol.

## Patentansprüche

1. Verfahren zur Herstellung von Polymerteilchen mit gleichmässiger Grösse mit einer gewählten endgültigen Teilchengrösse innerhalb des Bereichs von 1 bis 50  $\mu\text{m}$ , dadurch gekennzeichnet, daß man
  - a) ein frei radikalisch polymerisierbares wasserunlösliches Monomeres oder ein Gemisch von solchen Monomeren mit einer wässrigen Dispersion von Keimpolymerteilchen gleichmässiger Grösse kombiniert bis genügend Monomeres oder Gemisch von Monomeren kombiniert ist um die Teilchen auf eine gewählte Grösse wachsen zu lassen und worin das Monomere oder das Gemisch von Monomeren mit der wässrigen Dispersion von Keimpolymerteilchen (i) in Gegenwart eines Dispersionsstabilisators und eines öllöslichen frei radikalischen Polymerisationsinitiators (ii) bei einer Temperatur kombiniert wird, die wenigstens so hoch ist wie die, bei welcher der Initiator aktiviert wird und (iii) mit solcher Geschwindigkeit, daß eine Menge des Monomeren oder Gemischs von Monomeren gleich dem gesamten anfänglichen Gewicht der Keimpolymerteilchen mit der Dispersion über eine Zeitspanne von 45 bis 120 Minuten kombiniert würde; und
  - b) die Temperatur des oder der vereinigten Monomeren und der Teilchen wenigstens so hoch hält wie die, bei welcher der Initiator aktiviert wird bis alles Monomere polymerisiert ist
 wobei diese Stufen gegebenenfalls wiederholt werden, bis die gewählte Grösse gleich der gewählten endgültigen Teilchengrösse ist.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Geschwindigkeit, mit welcher das Monomere oder das Gemisch von Monomeren und die Dispersion kombiniert werden so ist, daß die Menge an Monomerem oder Gemisch von Monomeren gleich dem gesamten Anfangsgewicht der Keimpolymerteilchen mit der Dispersion über eine Zeitspanne von 60 bis 90 Minuten kombiniert wird.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Zugabegeschwindigkeit des Monomeren oder Gemisches von Monomeren so ist, daß das vorhandene freie Monomere oder Gemisch von Monomeren nicht 10 Gew.-% des momentanen Gewichts der Polymerteilchens übersteigt.
4. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die gewählte Grösse, die aus Stufe a) erhalten wird, 1,1

- bis 10 mal, vorzugsweise 1,5 bis 7 mal und am bevorzugtesten 2 bis 5 mal das anfängliche Volumen des Keimpolymerteilchens ist.
5. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Keimpolymerteilchen emulsionspolymerisierte Teilchen sind, die einen Anfangsdurchmesser von 0,01 bis 2 µm, vorzugsweise 0,05 bis 0,5 µm haben. 5
  6. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß die Keimpolymerteilchen Teilchen sind, die durch einmaliges oder mehrfaches Anwenden der Stufen a) und b) auf emulsionspolymerisierte Teilchen erzeugt sind. 10
  7. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Stabilisierungsmittel ausgewählt ist aus anionischen oberflächenaktiven Mitteln und nichtionischen oberflächenaktiven Mitteln. 15
  8. Verfahren nach Anspruch 7, dadurch gekennzeichnet, daß das Stabilisierungsmittel zusätzlich ein wasserlösliches Polymeres umfaßt. 20
  9. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Initiator eine Einstunden-Halbwertszeit-Temperatur von 60 bis 100°C hat. 25
  10. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß der Initiator ein Peroxid-Initiator, vorzugsweise Benzoylperoxid, oder ein Azo-Initiator ist. 30
  11. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Monomere oder Gemisch von Monomeren eines oder mehrere vinylaromatische Monomeren ist und gegebenenfalls vernetzendes Monomeres enthält. 35
  12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Monomere Styrol ist. 40
  13. Verfahren nach irgendeinem der vorhergehenden Ansprüche, dadurch gekennzeichnet, daß das Monomere oder Gemisch von Monomeren mit den Polymerteilchen in Gegenwart eines Porogens kombiniert wird. 45
  14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das Porogen in einer Menge von bis zu 50% vorliegt, wobei der Prozentsatz auf dem Gewicht von Monomerem oder Monomeren plus Porogen beruht. 50

15. Verfahren nach Anspruch 13 oder 14, dadurch gekennzeichnet, daß das Porogen Toluol, Xylol oder Methylisobutylcarbinol ist. 55

## Revendications

1. Procédé pour la fabrication de particules polymères de taille uniforme, ayant une granulométrie finale sélectionnée comprise entre 1 et 50 µm, qui comprend les étapes consistant à :

- a) combiner un monomère insoluble dans l'eau, polymérisable par polymérisation radicalaire à radicaux libres, ou un mélange de tels monomères, avec une dispersion aqueuse de particules de germes polymères de taille uniforme, jusqu'à ce que se soit combinée une quantité du monomère ou du mélange de monomères suffisante pour faire croître les particules jusqu'à une taille sélectionnée, et où le monomère ou le mélange de monomères est combiné avec la dispersion aqueuse de particules de germes polymères (i) en présence d'un stabilisant de dispersion et d'un amorceur de polymérisation radicalaire à radicaux libres soluble dans l'huile, (ii) à une température au moins aussi élevée que celle à laquelle l'amorceur est activé, et (iii) à une vitesse telle qu'une quantité du monomère ou du mélange de monomères égale au poids initial total des particules de germes polymères soit combinée avec la dispersion en un laps de temps compris entre 45 et 120 minutes ; et
- b) maintenir la température des particules et du ou des monomères combinés à une valeur au moins aussi élevée que celle à laquelle l'amorceur est activé, jusqu'à ce que la totalité du monomère soit polymérisée,

ces étapes étant éventuellement répétées jusqu'à ce que la taille sélectionnée soit égale à la granulométrie finale sélectionnée.

2. Procédé selon la revendication 1, dans lequel la vitesse à laquelle le monomère ou le mélange de monomères et la dispersion sont combinés est telle qu'une quantité de monomère ou de mélange de monomères égale au poids initial total des particules de germes polymères soit combinée avec la dispersion en un laps de temps compris entre 60 et 90 minutes.
3. Procédé selon la revendication 1 ou 2, dans lequel la vitesse de l'addition du monomère ou du mélange de monomères est telle que le monomère libre ou le mélange de monomères libres présent ne dépasse pas 10 % en poids par rapport au poids



des particules polymères instantané.

poids du ou des monomères plus l'agent porogène.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel la taille sélectionnée obtenue dans l'étape (a) représente 1,1 à 10 fois, de préférence 1,5 à 7 fois et mieux encore 2 à 5 fois le volume initial des particules de germes polymères. 5
5. Procédé selon l'une quelconque des revendications précédentes, dans lequel les particules de germes polymères sont des particules polymérisées en émulsion ayant un diamètre initial compris entre 0,01 et 2  $\mu\text{m}$ , de préférence entre 0,05 et 0,5  $\mu\text{m}$ . 10
6. Procédé selon l'une quelconque des revendications précédentes, dans lequel les particules de germes polymères sont des particules produites par application, une ou plusieurs fois, des étapes a) et b) à des particules polymérisées en émulsion. 15
7. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'agent stabilisant est choisi parmi les tensioactifs anioniques et les tensioactifs non-ioniques. 20
8. Procédé selon la revendication 7, dans lequel l'agent stabilisant comprend de plus un polymère soluble dans l'eau. 25
9. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'amorceur a une température de demi-vie, sur une heure, comprise entre 60 et 100°C. 30
10. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'amorceur est un amorceur peroxyde, de préférence un peroxyde de benzoyle, ou un amorceur azoïque. 35
11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le monomère ou le mélange de monomères est constitué d'un ou plusieurs monomères vinylaromatiques et comprend éventuellement un monomère réticulable. 40
12. Procédé selon la revendication 11, dans lequel le monomère est le styrène. 45
13. Procédé selon l'une quelconque des revendications précédentes, dans lequel le monomère ou le mélange de monomères est combiné avec les particules polymères en présence d'un agent porogène. 50
14. Procédé selon la revendication 13, dans lequel l'agent porogène est présent en une quantité allant jusqu'à 50 %, ce pourcentage étant basé sur le 55
15. Procédé selon la revendication 13 ou 14, dans lequel l'agent porogène est le toluène, le xylène ou le méthyl-isobutyl-carbinol.